Visible light-driven graphitic carbon nitride (g-C_3N_4) photocatalyzed ketalization reaction in methanol with methylviologen as efficient electron mediator

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ABSTRACT

Ketalization reaction, which is otherwise a typical acid catalyzed process, is herein firstly realized by a novel visible light driven photocatalytic reaction system with methylviologen (MV^{2+}) as an efficient electron mediator and graphitic carbon nitride (g-C_3N_4) as the visible light sensitizer. The photons utilization efficiency of g-C_3N_4 was maximized by simultaneous removal of the conduction band electrons and valence band holes by MV^{2+} and methanol, respectively. The turn over number of MV^{2+} reaches the remarkable high value of 31201/hour, with 72.7 mmol of cyclohexanone dimethyl ketal production in 1 h. The design strategy presented in this work could inspire the development of new and highly efficient photocatalytic reaction systems for broader purposes than usually expected.

1. Introduction

Semiconductor photocatalyzed organic functional groups conversion reactions have attracted increasing attention in recent years. *Via* this route, the abundant solar light can be directly employed as the energy source to drive the chemical reactions. Meanwhile, the novel reaction mechanism involved also contributes positively to the organic synthesis area [1–8]. Ketalization reaction is an effective way for protecting the carbonyl group during organic synthesis. Moreover, some of the ketals are valuable fine chemicals, such as cyclohexanone dimethyl ketal, which is a dehydration agent and also is a valuable intermediate for synthesis of perfumes and agricultural chemicals [9,10]. In terms of the production of dimethyl ketals, expensive reactant (trimethyl orthoformate), corrosive acid catalysts, and special reactors with water separation devices have to be involved to obtain satisfied yields and purities [9,11]. A novel, environmental benign photocatalytic method for ketalization of ketones with methanol is thereby highly desirable from the perspectives of both basic science and practical application.

Graphitic carbon nitride (g-C_3N_4), which is a conjugated polymer semiconductor with band gap of 2.7 eV, has raised intensive

research interest, due to its physicochemical stability, metal-free composition made up from abundant elements, and most importantly, its visible light sensitivity [12–18]. However, achieving notable efficiency is challenging, because of the mutual influences and kinetic coupling within the complex electron transfer processes. Specifically, in semiconductors photo-catalyzed chemical conversion reactions, electrons are firstly exited to the conduction band by photons, leaving the oxidative holes in valence band; and these photo-generated charge-carriers, if not recombined in loss processes, drive the organic conversion reactions *via* electron and hole transfer with the reactants. Low conversion efficiency usually results from unwanted charge recombination, back electron transfer (BET) or a missing rate balance of the chemical reactions of electron and hole, *i.e.* the system has to "wait" for the slower reaction [19–23]. Interestingly, in bio-photosynthesis, the multisteps electrons transfer processes from PS II (Photosystem II) to PS I (Photosystem I) and PS I to $NADP^+$ (Nicotinamide Adenine Dinucleotide Phosphate) are able to realize high quantum yields [24,25]. This was mimicked *in vitro* by coupling semiconductor photocatalysis with enzyme biosynthesis *via* NAD^+ as an electron mediator, and the reported kinetic rates of 5 mmoles per hour speak for bio-like photon-to-reaction efficiencies exceeding 20% [26,27]. Accordingly, the improvement of the efficiency of the artificial photocatalytic reactions by virtue of a kinetically favourable electron mediator is particularly promising.

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Methylviologen (MV^{2+}) is a bipyridylium cation, which can capture one electron and change to reduced methylviologen (MV^+) (MV^{2+}/MV^+, −0.45 V $vs.$ NHE) [28–31]. The quantum yield for MV^+ generation with CdSe/CdS (Dot-in-Rod nanostructure) as photosensitizer could reach nearly unity [32]. MV^+ readily donates one electron in the presence of Pt nanoparticles for hydrogen production in $Ru(bipy)^{2+}$ and CdSe/CdS photocatalytic systems with sacrificial electron donors [32,33]. Some enzymes and cofactors, such as formate dehydrogenase, flavin mononucleotide, and hydrogenase are also able to receive electron from MV^+ and initiate the following reduction reactions [34–36].

Extending these observations to the more feasible graphitic carbon nitride, it is reasonable to expect high photocatalytic conversion efficiency, if the MV^{2+} could promptly capture the conduction band electrons on the surface of g-C_3N_4 particles. The left-alone valence band holes in carbon nitride possess strong oxidative power (1.40 V $vs.$ NHE), which can be instrumentalized to drive many chemical conversion reactions [17,37,38]. Methanol, as a potential hole scavenger, can in principle quickly donate electrons to the hole and be oxidized to formaldehyde via the intermediate step of methoxy radical formation [39–41]. This methoxy radical is an active species, and could be a useful building block in organic synthesis, especially for C—O bond formation.

Herein, we apply the combination of the MV^{2+}/MV^+ redox couple and methanol in the g-C_3N_4 system to explore a novel photocatalytic ketalization reaction of ketones. This reaction system is highly efficient when the positive and negative charges from g-C_3N_4 are taken up by MV^{2+} and methanol, respectively, with similarly high rates.

2. Experiments

2.1. g-C_3N_4 synthesis

g-C_3N_4 photocatalyst was synthesized with urea as the precursor in a furnace with nitrogen atmosphere. The urea was heat to 600 °C at a ramp rate of 5.5 °C/min, and the polymerized at 600 °C for 3 h. The as prepared yellow product was ground into fine powder followed by washing with methanol and water for 3 times each. The sample was then dried in the freeze-drier for 12 h. The yellow g-C_3N_4 powder was dried at 120 °C before used for reaction.
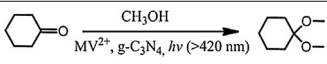
2.2. Photocatalytic reactions

The standard reaction conditions: Calculated amount of substrate, methylviologen chloride, g-C_3N_4, and toluene was mixed with anhydrous methanol in a 50 mL Pyrex glass reactor. The reactor was then sealed and connected to the Schlenk line, the reactor was flushed with nitrogen flow for 20 min. Then the reactor was placed on a magnetic stirrer, irradiated by 100 W white LED (10000 lm). A high power axial fan installed near the reactor kept the reactor at room temperature during light irradiation. Product was analysed by Agilent GC (6890) −MS (5975) with HP-5 capillary column.

3. Results and discussion

The typical SEM image, XRD pattern, and UV–vis absorption spectra of the graphitic carbon nitride are shown in Fig. S1. g-C_3N_4, with building block of tri-s-triazine, is electron rich and intrinsically negative, which is favourable for the surface absorption of the positive MV^{2+} [12]. As shown in Table S1, zeta potential of g-C_3N_4 in water and methanol is − 27.0 and − 0.4 mV, respectively. With the addition of the MV^{2+} in the solvents, zeta potentials positively shift to − 7.5 and 28.5 mV in water and methanol, respectively, indicating

Table 1
Control experiments of the photocatalytic ketalization of cyclohexanone with methanol on g-C_3N_4.

Entry	Photocatalyst	Visible light Irradiation	MV^{2+} (µmol)	Conversion (%)
1[a]	g-C_3N_4	Yes	2.33	92.4
2[b]	g-C_3N_4	No	2.33	0
3	g-C_3N_4	Yes	0	0
4	–	Yes	2.33	0
5	TiO_2	Yes	2.33	0
6[c]	g -C_3N_4	Yes	2.33	0

[a] Standard reaction condition: 30 mg g-C_3N_4, 10 mmol cyclohexanone, 48 mL anhydrous methanol, nitrogen atmosphere, 1 h light irradiation with 100 W LED (λ> 420 nm), and room temperature (RT).
[b] The dark reaction was at 60 °C for 3 h.
[c] The reaction was in anhydrous isopropyl alcohol (IPA).

the surface adsorption of MV^{2+} on g-C_3N_4. The surface absorption of MV^{2+} on g-C_3N_4 directly promotes the electron transfer process between them under photon excitation. As shown in Fig. 1a, MV^{2+} is quickly reduced upon the visible light irradiation, showing fast rising of the distinctive absorption peak at λ = 605 nm. Meanwhile, after photo-irradiation, g-C_3N_4 in the dark blue solution shows the original yellow colour, indicating MV^+ is more weakly absorbed on g-C_3N_4 surface (Fig. 1b and c). The spatial separation of the photo-induced charges could hinder direct reoxidation of the MV^+ by the hole and contribute to the efficiency of this photocatalytic reaction system.

The reaction was successfully confirmed by the production of 1,1-dimethoxycyclohexane via one hour photocatalytic ketalization of cyclohexanone with 92.4% conversion and >99% selectivity (Table 1, entry 1; Fig. S2). To clarify the roles of each part in this reaction system, a series of control experiments was performed employing cyclohexanone as the substrate (Table 1). Without visible light irradiation, there was no reaction even at 60 °C (Table 1, entry 2), excluding the possibility of a thermal addition process. The control reaction under visible light irradiation without MV^{2+} gave no product, showing the critical role of the catalytic amount of 2.33 µmol MV^{2+} for the system (Table 1, entry 3). When g-C_3N_4 was removed from the system or substituted by the visible light inactive TiO_2 (Anatase), there was no product detected after 1 h visible light irradiation (Table 1, entries 4 and 5), demonstrating the role of g-C_3N_4 as visible light sensitizer in this system. To deduce the details of the reactions initiated by valence band hole, isopropyl alcohol (IPA), which is a secondary alcohol and could also work as hole scavenger, was employed for a comparison [42]. As indicated by the blue color of the reaction mixture, MV^+ was produced in the reaction solution, demonstrating that the conduction band electrons and valence band holes had been trapped by MV^{2+} and IPA, respectively. However, there was no cyclohexanone conversion, which may due to the difference in the intrinsic reactivity of the methoxy and isopropoxy radicals (Isopropoxy radical changes to 2-hydroxy-2-propyl radical immediately after formation by hydrogen abstraction from isopropyl alcohol) [43,44]. The selectivity on the alcohol hole scavenger in the reaction system confirms again that the ketalization reaction herein is not acid-initiated, but photon-initiated. All the control experiments state that visible light, g-C_3N_4, and the presence of the cofactor MV^{2+} are all indispensable to the photocatalytic ketalization reaction.

Based on the analysis of the control experiments, we propose a possible reaction mechanism of the photocatalytic ketalization reaction with methanol on g-C_3N_4 (Scheme 1). Under visible light irradiation, methanol is oxidized to methoxy radical by the photo-generated hole. As an active species, the methoxy radical reacts
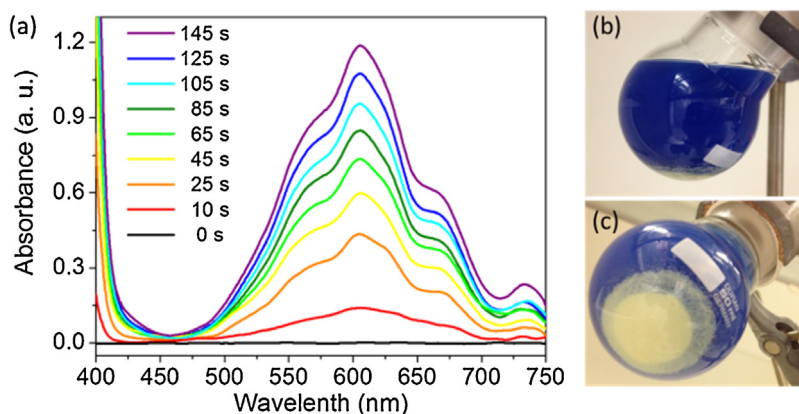
Fig. 1. (a) UV–vis spectra of nitrogen flushed anhydrous methanol containing MV^{2+} and g-C_3N_4 before and after visible light irradiation. Side-view (b) and bottom-view (c) photos of the reactor after 30 min visible light irradiation. In both cuvette and reactor, the reaction condition: 1 mM MV^{2+} in anhydrous methanol with 0.6 g L^{-1} g-C_3N_4; light source, 100 W LED ($\lambda > 420$ nm).
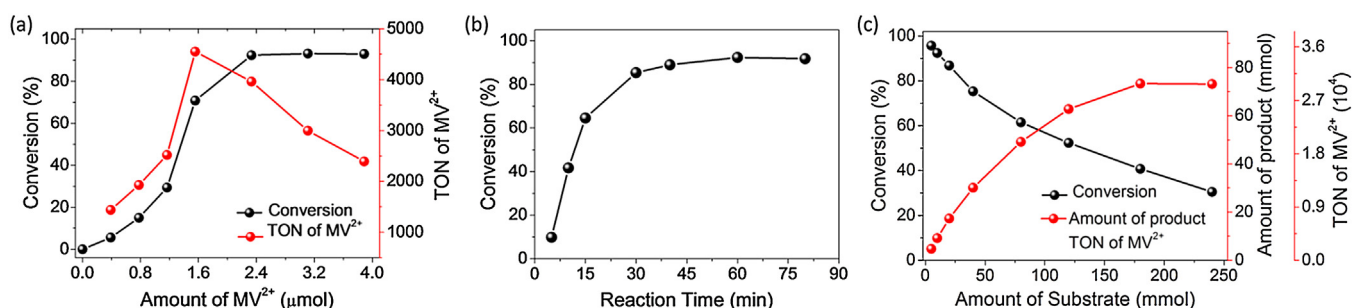

Fig. 2. (a) Variation in cyclohexanone conversion and turn over number (TON) of MV^{2+} with the amount of MV^{2+} in 1 h photocatalytic ketalization reaction. The amount of substrate is 10 mmol. (b) Profile of conversion versus the reaction time in photocatalytic cyclohexanone ketalization. The amount of substrate and MV^{2+} in the reactions is 10 mmol and 2.33 μmol, respectively. (c) The cyclohexanone conversion, amount of ketalization product, and turn over number (TON) of MV^{2+} of the reactions with a series of substrate concentrations. The amount of MV^{2+} is 2.33 μmol and the total volume of methanol and cyclohexanone is 49 mL in each reaction. Other common reaction conditions: 30 mg g-C_3N_4, nitrogen atmosphere, room temperature, toluene as the internal standard, and visible light irradiation by 100 W LED ($\lambda > 420$ nm).
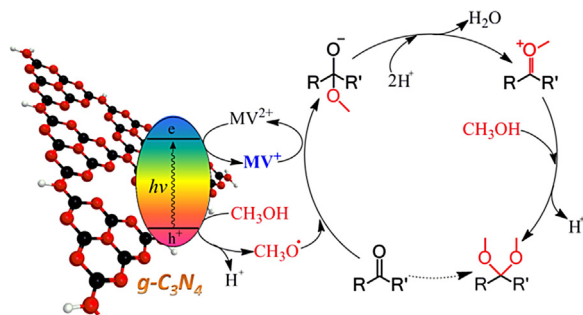
Scheme 1. Proposed reaction mechanism of the MV^{2+} mediated photocatalytic ketalization of the ketones with methanol under visible light irradiation on g-C_3N_4.

with carbonyl group of the ketone and produces a radical adduct, followed by receiving one electron from MV^+. The subsequent steps involve protons transfer, elimination of water, and nucleophilic attack of the resonance-stabilized intermediate by methanol. The ketal then forms as the final product.

To further promote the understanding on the proposed reaction mechanism, the variation in the conversion with MV^{2+} and cyclohexanone concentrations was studied. As shown in Fig. 2a, at low MV^{2+} concentration, the amount of photocatalytic ketalization product sharply increases with MV^{2+} concentration in the system, indicating the rate determining character of MV^{2+} in electron transfer from carbon nitride to the reaction intermediate. The curve shows a plateau when the amount of MV^{2+} in the reaction is higher than 2.33 μmol, suggesting that under such reaction

condition, the conduction band electrons output rate is balanced to the other reactions and is not rate-determining, anymore. An interesting volcano-shaped curve of TON versus concentration of MV^{2+} is observed. With 1.56 μmol MV^{2+} as electron mediator and 10 mmol cyclohexanone as substrate, the TON of MV^{2+} reaches a notable peak value of 4552/hour. It confirms that MV^{2+} is running as a highly efficient shuttle, continuously feeding electrons to the cyclohexanone ketalization reaction steps. Fig. 2b shows the variation in the cyclohexanone conversion with the reaction time. The reaction system converts 9.9% of the cyclohexanone in the first 5 min. While after that, the conversion at 10 and 15 min is 41.7% and 64.4%, respectively. Obviously, there is an induction period in the first few minutes (Fig. S3a). During this short induction period, methoxy radicals and MV^+ ions are produced in the system, which are the necessities for the ketalization of cyclohexanone (Scheme 1). After the induction period, the conversion data plots are well fitted according to the pseudo-first order kinetics with an apparent reaction rate constant of 0.0016 s^{-1} (Fig. S3b), indicating that the methoxy radical and MV^+ are adequate in the system for cyclohexanone conversion, i.e. the reaction rate here is determined by the reactivity and concentration of the ketone, rather than the transfer of the photo-induced charges by MV^{2+} and methanol. To maximize the photons-to-molecule conversion in this reaction system, the concentration of the substrate (cyclohexanone) is further increased. As shown in Fig. 2c, with the increase of the substrate concentration, the amount of the ketalization product increases rapidly, although the conversion decreases from 95.7% with 5 mmol substrate to 40.8% with 180 mmol substrate. This suggests that the rising concentration allows the substrate to capture higher amount

of short-lived methoxy radicals, which otherwise would further react to formaldehyde, but that then the chosen reaction time is not sufficient to allow complete conversion. Moreover, as indicated by the blue color of the reaction, MV^+ is always present in the solution, and the formation of a higher amount of intermediate radical adduct reasonably improves the reaction rate. In one hour photocatalytic reaction with 180 mmol cyclohexanone and 2.33 μmol MV^{2+}, 72.7 mmol of the 1,1-dimethoxycyclohexane is produced, corresponding to a remarkably high MV^{2+} TON of 31201/hour. As stated by the color of the reaction mixture, MV^+ concentration of the reaction mixture with 180 mmol cyclohexanone is lower than that with 10 mmol substrate, which is due to the role of MV^+ as electron donor for the catalytic cycle (Fig. S4). It convincingly demonstrates again that MV^{2+}/MV^+ couple serves as a highly efficient electron mediator. Further increase of the substrate amount to 240 mmol, no further increase is observed, stating that the upper kinetic limit of this system under the given reaction condition has been reached.

The photocatalytic ketalization reactions with methanol have been extended to a series of aliphatic ketones, and the data are shown in Table 2. Various aliphatic ketones are selectively converted to their corresponding dimethyl ketals with high reaction rate. One hour photocatalytic reaction with 4-methylcyclohexanone as substrate affords 8.00 mmol 1,1-dimethoxy-4-methylcyclohexane, with MV^{2+} TON of 3433/hour (Table 2, entry 1). Methyl group substitution on the alpha-C of cyclohexanone causes lower conversion. With 2-methylcyclohexanone as substrates, 4.31 mmol of the ketalization product is produced in one hour, and the TON of MV^{2+} is 1850/hour (Table 2, entry 2). For the acyclic ketone, the position

of the carbonyl group and the length of the carbon chain affect their ketalization reactivity. Shorter carbon chains and carbonyl group being at the end of the chain are good for conversion. The reactions with 3-methyl-2-butanone and 2-hexanone as substrates show higher conversion than that with 3-pentanone as substrate (Table 2, entries 3–5). With acetone as the substrate, 5.46 mmol 2,2-dimethoxypropane is produced in one hour photocatalytic

Table 2
Photocatalytic ketalization of a series of aliphatic ketones with methanol on g-C_3N_4.[a]

| Entry	Substrate	Product	Product Amount (mmol)	Conversion (%)	TON
1			8.00	93.9	3433
2			4.31	50.6	1850
3			3.07	36.0	1318
4			1.90	22.3	815
5			2.72	31.9	1167
6			5.46	64.1	2343

[a] Reaction condition: 8.6 mmol substrate in 48 mL anhydrous methanol, 30 mg g-C_3N_4, nitrogen atmosphere, room temperature (RT), visible light irradiation for 1 h. Amount of MV^{2+}, 2.33 μmol; Conversion and selectivity are determined by GC-FID with toluene as the internal standard.

Table 3
Photocatalytic ketalization of a series of aromatic ketones with methanol on g-C_3N_4.[a]

Entry	Substrate	Product	Product Amount (mmol)	Conversion (%)	TON
1			0.77	9.1	22
2			1.92	22.6	55
3			1.76	20.7	50
4			2.18	25.6	62
5			2.26	26.5	65
6			2.38	27.9	68
7			3.05	35.8	87
8			2.78	32.6	79

[a] Reaction condition: the same to that in Table 2, except the amount of MV^{2+} is 35 μmol.

ketalization, and the TON of MV^{2+} is calculated to be 2343/hour (Table 2, entry 6).

Compare to the aliphatic ketones, the aromatic ketones show relatively lower activities in the photocatalytic ketalization reaction. As shown in Fig. S5a, the acetophenone conversion can be increased with the concentration of MV^{2+}, and here the maximum conversion is obtained with 35 μmol MV^{2+} in the reaction system, in which one hour reaction produced 1.92 mmol of the ketal. This increased effective concentration clearly reflects one order of magnitude lower reactivity of MV^+ with the aromatic intermediate. With the MV^{2+} amount at a constant value of 35 μmol in each reaction, the product amount also increases with the substrate concentration (Fig. S5b). In particular, after 1 h visible light irradiation of the reaction mixture with 3.5 mol L^{-1} acetophenone, the amount of the product reaches the highest value of the series, 6.37 mmol.

Various substituted acetophenone are converted to their corresponding ketals with high selectivity of 99% (Table 3). Electron donating substituents of the carbonyl group retard the reaction rate, while the electron withdrawing substituents do the opposite. Further information on the photocatalytic ketalization reaction mechanism is obtained by correlating the substituent constants and the relative reaction rates in a Hammett plot (Fig. S6). The reaction constant (ρ) of 0.582 states that the reaction is susceptible to the electronic perturbation, and that an anionic intermediate is involved in the rate determining step, which is consistent to the proposed mechanism [45].

4. Conclusion

In summary, *via* a novel photocatalytic route, ketalization reaction with high reaction rate and selectivity is realized. In this reaction system, carbon nitride is used as a visible light sensitizer, and the photo-induced charges are efficiently removed from g-C_3N_4 surface by MV^{2+} as the electron mediator and methanol as the hole scavenger. The spatial separation of the photo-induced charges maximize the photo-utilization efficiency of g-C_3N_4; and kinetic experiments show that all reactions rates in this system can be balanced by system engineering within reasonable reactant concentrations. As such, with a catalytic amount of 2.33 μmol MV^{2+} as electron mediator, 72.7 mmol of the 1,1-dimethoxycyclohexane can be produced from one hour of photocatalytic cyclohexanone ketalization, corresponding to a remarkable high MV^{2+} TON of 31201/hour. This work expands the scope of the semiconductor photocatalytic organic conversion reactions, and also sheds light on more general strategy to design novel and efficient photocatalytic system for solar energy conversion.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2017.02.044.

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